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DETECTION TECHNIQUES FOR TENUOUS PLANETARY ATMOSPHERES

Thirteenth Six-Month Report  
for the period

1 July 1969 - 31 December 1969

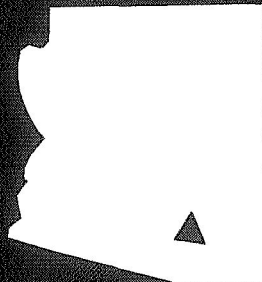
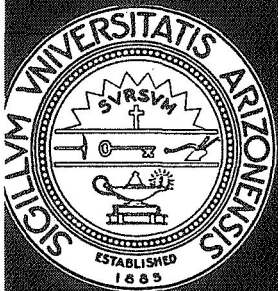
For the

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

Grant NGL-03-002-019

Stuart A. Hoenig  
Principal Investigator

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COLLEGE OF ENGINEERING  
THE UNIVERSITY OF ARIZONA  
TUCSON, ARIZONA

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Stuart A. Hoenig  
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John Ashcraft  
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## DETECTION TECHNIQUES FOR TENUOUS PLANETARY ATMOSPHERES

### I. Introduction, Abstract, and Summary

This report will cover the work performed from 1 July 1969 through 31 December 1969 on Grant NGL-03-002-019 between the University of Arizona and the National Aeronautics and Space Administration.

This contract was set up to support the development of new types of detectors for analysis of planetary atmospheres. Initially, the interest was in detectors for use under partial vacuum conditions; recently, the program has been extended to include detectors for use at one atmosphere and adsorption systems for control and separation of gases.

Results to date have included detectors for  $O_2$  and  $H_2$  under partial vacuum conditions (Publications 1, 3, 4). Experiments on detectors for use at higher pressures began in 1966, and systems for CO,  $H_2$ , and  $O_2$  were reported in 1967 and 1968 (Publications 8, 12). In 1968 studies began on an electrically controlled adsorbent. It was demonstrated that under proper conditions a thin film of semiconductor material could be electrically cycled to adsorb and desorb a specific gas. This work was extended to obtain quantitative data on the use of semiconductors as controllable adsorbents (Publication 12).

In 1968 a new technique for dry replication and measurement of the thickness of thin films was developed. A commercial material, Press-O-Film, was shown to be satisfactory when properly used. This technique

is most useful for studies of semiconductor thin films where normal interference techniques are not practical because of the nonreflective nature of the film (Publication 13).

In 1969 studies began on a corona discharge detector for water vapor. This system was shown to be rapid in response, suitable for continuous low power operation and reasonably linear in output (on a logarithmic plot) from 10% R.H. to 95% R.H.

The electroadsorption phenomena reported in 1968 (Publication 12) was extended to bulk ZnO samples by using a gas chromatograph. The objective of developing a controllable electroadsorbent is slowly being realized.

## II. Summary of Work in the Past Six Months

### A. CO or H<sub>2</sub> Adsorption on Hot Palladium

Studies of the reaction of CO or H<sub>2</sub> with hot palladium indicate that the change in positive ion emission that occurs when these gases contact the metals is due at least partially to removal of a surface layer of sulfur and carbon. This layer of impurities has been demonstrated to be due to S and C diffusing from the interior of the metal to the surface.

### B. Corona Discharge Humidity Detector

The current generated in a point-to-plane corona discharge was shown to be dependent on the ambient water vapor pressure. The use of a multipoint brush and an ultraviolet source stabilizes the system and maintains sensitivity over a wide range of R.H. The system has been repackaged for use in field studies.

C. Electroadsorption of  $O_2$  on ZnO

A new system has been designed and built to make use of the gas chromatograph. Most of the effort has been devoted to finding an optimum system for holding the ZnO, applying the electric field and introducing the gas. The system is new and no results are available at this time.

D. Electron Emission from Thoriated Tungsten as a Detector for Trace Quantities of Water Vapor

Some years ago it was shown that the electron current from hot tungsten was dependent upon the partial pressure of water vapor. The application of this system for detection of water vapor on Mars has become a possibility, and we have been looking at this reaction again in the presence of high (5 torr) pressures of  $CO_2$ . There have been problems with filament burn-out because of  $CO_2$ /tungsten reactions, but we are still working on the project with the hope of operating at lower temperatures where  $CO_2$ /W reactions will not occur.

E. Other Activities in the Laboratory

The ARPA-sponsored studies on the relationships between fatigue and subsequent exo-electron emission are continuing. We have shown that if a metal is fatigued to some fraction of its total life and then heated gently, it will emit exo-electrons. This electron current can then be related to the fatigue history of the specimen.

In November 1969, Mr. Christian Savitz joined the group as a part-time technician on the ARPA project. His work has been a significant contribution to the laboratory.

### III. Individual Project Reports

#### A. CO or H<sub>2</sub> Adsorption on Hot Palladium

Richard Pope and John Ashcraft

These studies have been going on for some four years; in 1966 we showed that when CO or H<sub>2</sub> contacted hot Pd, a current of positive ions was emitted. This positive ion current was dependent on the partial pressure of H<sub>2</sub> or CO and could be used as a detector for these gases.

The phenomenon behind this positive ion emission has been elusive. Originally we suggested that positive ions of H<sup>+</sup> or CO<sup>+</sup> were generated on the Pd surface, but a simple thermodynamic argument killed that idea. When a mass spectrometer became available, we determined that the emitted ions were sodium and potassium initially present as impurities in the palladium.

The next question was, of course, why should the ambient gas affect the ion emission? Three possible processes were suggested for this reaction:

1. The CO or H<sub>2</sub> might dissolve in the palladium, expand the palladium lattice and permit more Na and K to diffuse to the surface.
2. The CO or H<sub>2</sub> might change the Pd work function and thereby increase the fraction of Na and K emitted as ions rather than atoms.
3. If the Pd surface was initially covered by a layer of some material which partially blocked the flow of Na and K, a gas that reacted with this surface layer (and removed it) would increase the Na<sup>+</sup> and K<sup>+</sup> ion current.

These questions have been investigated by Mr. Richard Pope as part of his thesis work for the M. S. degree. The experimental system is shown in Figure 1. With the EAI Quad - 250 mass spectrometer and associated apparatus, it was practical to measure the gas pressure, composition, ion emission and palladium temperature as a function of time.

In a series of experiments we have observed:

1. The emitted positive ion spectrum as a function of time, ambient gas composition and pressure.
2. The changes in the system gas composition as a function of palladium temperature.

The results of Item 1 above indicate that only the ions of Na, K, and Ca are present. The order of abundance is that listed above; these elements are thought to be present as initial impurities in the palladium.

The total ion current is a function of ambient gas pressure and displays a strange hysteresis behavior as the pressure changes. The effect is observable with  $H_2$ ,  $N_2$ , and  $O_2$ . Typical results are shown in Figure 2. The ion current is lower on the increasing part of the cycle than on the decreasing part. The loop width is largest at a pressure of 0.1 to 10 torr and then closes at higher and lower pressures.

At the moment we have no explanation for this data. The hysteresis with hydrogen might be due to solubility, but Smith (Reference 1) indicates that Pd does not show hysteresis in adsorption at 800°C. To the best of our knowledge this phenomenon has not been reported in the literature for  $H_2$ ,  $O_2$ , or  $N_2$  on Pd at 800°C. It may well be that positive ion emission is a more sensitive test for solubility than those presently in use.

The appearance of hysteresis in adsorption, with an isotherm that is lower when measured with increasing pressure than with decreasing pressure, has been discussed by de Boer (Reference 7). He suggests that microporosity may be the cause of this phenomenon. This agrees with the discussion of Reference 1, page 84, which suggests that  $H_2$  is adsorbed by Pd and opens fissures; these fissures (microporosity) permit the  $H_2$  to escape easily when desorption begins. This idea that the lattice is opened by adsorption may be driving force behind Figure 2 where higher ion currents are observed during desorption. This topic will bear further investigation.

The observations of changes in ambient gas composition, when hot palladium is present, require some discussion of the experimental technique before presentation.

For an experimental run, the Pd was outgassed at  $1000^\circ\text{C}$  for 60 minutes at  $10^{-8}$  torr and then cooled to  $23^\circ\text{C}$ . The residual gas was analysed, and then  $H_2$  or CO was introduced and the pressure stabilized. The gas was analysed again, and the Pd was heated to  $800^\circ\text{C}$ . The ambient gas was analysed continuously for some 19 minutes as the CO or  $H_2$  reacted with the hot Pd. Each experiment run was repeated at least three times.

The results are presented in normalized form. This normalization was necessary because the mass spectrometer varied slightly in sensitivity from run to run. This in turn induced changes in peak height for all the mass peaks. In our results this all-mass-peak increase has been normalized out. Certain mass peaks were found to increase by factors considerable above the all-mass-peak average. It is these mass peaks that



we shall be concerned with. In Figure 3 we show the mass peaks that increased more than the all-mass-peaks average. The delta factor in Figure 3 shows the increase in each mass peak as a fraction of original peak height. We suggest that some of these peaks represent compounds generated by reactions between the ambient CO or H<sub>2</sub> and impurities that had diffused from the interior to the surface of the palladium. Impurity diffusion of carbon and sulfur on palladium has been reported by Tracy and Palmberg (Reference 2). These impurities could not be removed by heating alone. Carbon could be removed by heating to 900°C in  $5 \times 10^{-7}$  torr of oxygen. Removal of sulfur required argon-ion bombardment for days, indicating the strong bonding between sulfur and palladium.

To compare our data Figure 3 with that of Reference 2, we must look at the peaks at mass 44(CO<sub>2</sub>), 60(COS), and 64(SO<sub>2</sub>). The spectrum of CO/Pd shows significant peaks at mass 44, 60, and 64. (The peaks at mass 35, 45, 46, 47, etc., are hydrocarbons produced by the catalytic action of the hot Pd filament.) The H<sub>2</sub>/Pd spectrum shows significant peaks at mass 60(COS) and 64(SO<sub>2</sub>), but the expected peak at 34(H<sub>2</sub>S) is not present. All we can suggest at the moment is that H<sub>2</sub> somehow induces reaction between sulfur and carbon on the palladium and residual CO in the vacuum system.

More experiments will be run in the next six months. At the moment we can only propose that the change in positive ion current from palladium, in the presence of H<sub>2</sub> or CO, is due to an expansion of the Pd lattice and to the removal of a surface layer of carbon and sulfur.

Other aspects of the CO or H<sub>2</sub> versus hot Pd reaction have been investigated by Mr. John Ashcraft. Mr. Ashcraft's work was discussed in some detail in our last report; in that report, we indicated that the CO or H<sub>2</sub> versus Pd reaction produced a thermal pulse during adsorption at low (200°C) temperatures. This thermal pulse was associated with the adsorption isotherm of these gases on palladium.

In the last report we mentioned the observation of exo-electrons during adsorption of H<sub>2</sub> or CO on Pd. The emission of electrons during adsorption has been reported elsewhere for O<sub>2</sub> on Ni (Reference 4). The question of interest is "Is exo-electron emission a necessary part of the reaction, or is it just something that happens when adsorption occurs?"

Some very preliminary experiments by Mr. Ashcraft indicate that external electric fields can affect exo-electron emission and the CO/Pd adsorption reaction. More work in this area is needed before conclusions can be drawn about this effect, but if we can demonstrate that electric fields can affect adsorption, this will be a most significant discovery.

#### B. Corona Discharge Humidity Detector

Mark Carnes and David Bents

In our last six-month report, we discussed the development of a corona discharge humidity detector. The detector responded rapidly to changes in relative humidity, and the output current varied over some three orders of magnitude as the relative humidity changed from 10% to 90%.

In the last six months, a major effort by Mr. Carnes and Mr. Bents has been devoted to first repackaging the system in a form suitable

for field applications, second to finding the optimum configuration, and third to gaining understanding of the physical operation of the system.

The repackaging of the system and the testing process have been quite successful. The system is shown in Figure 4. The outer tube is 2-3/4" OD steel, the inner spacers are Teflon, and the brush is tungsten with 50 points. The UV light is enclosed in a quartz tube through which air is passed. This removes the heat generated by the UV light. In the past, this heat raised the temperature of the air as it passed through the system and effectively changed the relative humidity.

This "quartz-tube" technique has solved a most puzzling problem-- why the system would not operate at low flow rates. In the past, a large thru-put of air was needed apparently to remove the heat generated by the UV lamp. The new system operates at low flow rates (0.5 scfm or less), and we feel that this will be a significant advantage in field operations where fan power is limited.

A typical calibration curve is shown in Figure 5. The cross-hatched area indicates the spread in the data for three separate runs on three days when the barometric pressure varied over a range of about 1.5 inches of mercury. This spread is thought to be due primarily to the pressure sensitivity of the phenomenon itself; however, there is some scatter in the data because of the calibration techniques which makes use of wet and dry bulb thermometers. Our tables (Reference 5) are the best available, but it is sometimes necessary to interpolate, and this introduces an uncertainty factor. All of these errors are lumped together in the cross-hatched region in Figure 5.

The data of Figure 5 extends only to a R.H. of 70% because most of our effort has been devoted to developing an optimal system for the 10-50% R.H. range. In view of the fact that the system responds much faster than we can change the relative humidity, we feel that the results of Figure 5 are encouraging. We have taken data below 5% R.H.; the detector works quite well, but we do not believe in using wet bulb data below 10% R.H. in our application.

In the next six months, we will work on extending the range, investigating the effect of ambient barometric pressure, and developing an improved calibration system.

The other question that remains is that of understanding how the device works. Here we have made no effective progress at all. The UV light seems to be necessary if we are to have sensitivity below 30% R.H., but we don't know why. All we can say, at this time, is that we will try to find a graduate student to study this process for an M. S. thesis. For the present, Mr. Carnes will continue with the test program as part of his work on an undergraduate term project.

As a thought for the future, it is worth commenting that all conventional humidity detectors require a fan or pressure to pull air through them. In principle, a Corona Discharge System could be self-actuating because air would be pushed through the system by the Electric Wind Effect. A system of this type would require only high voltage, low current, power and could operate in a remote area for months without attention. A proposed detector of this type is shown in Figure 6. If any NASA group expresses interest in this technique, a simple working model to test feasibility can be built quite easily.

C. Electroadsorption of  $O_2$  on ZnO

Brad Frazier

In our earlier reports we discussed the electroadsorption of oxygen type gases on ZnO. It was demonstrated that ZnO could serve as a controlled and specific adsorbent but the application of this effect required more study and development. To further this work, we purchased a Hewlett-Packard model 700 gas chromatograph.

Mr. Frazier joined the group during the summer of 1969, and he has been working on the GC as part of his M. S. thesis program. Mr. Frazier has done a great deal of work on setting up this instrument for the ZnO experiment. A measure of this is the fact that graduate students in other departments are asking him for help with their GC problems.

Our studies in the last six months have been in two areas.

1. To find a better way of supporting the ZnO in thin layers for maximum ZnO/gas exposure. The most promising material to date is a ZnO coated paper donated through the kindness of Dr. Sam Schoenfeld of the New Jersey Zinc Company.
2. The other topic of present interest is the measurement of the separation capability of the ZnO system for  $O_2/N_2$  or  $O_2/Ar$  mixtures. We feel that the first application of this adsorption system might well be in gas chromatography where separation of  $O_2/Ar$  mixtures is a problem.
3. A more distant but important area of interest is that of catalysis. If we can control adsorption phenomena on ZnO, the step to control of catalysis is direct because catalysis depends upon adsorption.

The experimental system is built around the ZnO reaction tube which is shown in Figure 6. The ZnO is held on a white bond paper by a proprietary New Jersey Zinc Company process. The inner electrode is a brass screen, and the outer electrode is a thin film of stannous oxide.

The gas chromatograph H-P-700 is set up in an unusual way and will be described in some detail. The flow diagram for the GC is shown in Figure 7. The detector is a standard thermal-conductivity wheatstone bridge arrangement. The columns are porapak Q, diataport, and a molecular sieve. Operating parameters normally used are as follows:

Oven Temperature	100°C
Detector Temperature	130°C
Detector Current	200 mA
Carrier (Helium) Flow	50 ml/min

The helium flow passes through two gas sampling valves and into the porapak Q column. The column is external to the oven and at ambient temperature. The flow next goes through the back side of the detector and into the oven. In the oven are located the diataport and molecular sieve columns which are at 100°C.

The flow finally ends by passing through the front of the other side of the bridge detector. Note that the injection port is completely bypassed. This is done to decrease the diffusion of sample gas along the helium flow.

Upon injection of a slug of sample gas, the helium flow forces it into the first column, porapak Q. In this column CO<sub>2</sub> is resolved from the other gases. In the oven, the oxygen and CO are separated in the two

remaining columns. The oxygen comes out first while CO takes about 8 minutes to pass through the detector. An interesting feature of this flow system is the fact that the output from the detector changes sign as the various sample gases come through. The detector output is integrated by an op-amp integrator circuit to permit an accurate comparison between the composition of the gas flowing into the reaction system with that flowing out.

The experiments to date have involved running a mixture of a carrier gas (helium) and various reactant gases ( $O_2$ , CO, etc.) through the ZnO reaction system. The gases are sampled going in and coming out of the ZnO chamber. Results to date indicate that adsorption/desorption can be observed but no catalytic reactions have been seen. This is disappointing but not surprising because other investigators (Reference 6) have indicated that no catalytic action occurs at room temperature.

The system is being modified to permit heating of the catalyst and more comprehensive experiments on electroadsorption.

D. Electron Emission from Thoriated Tungsten as a Detector for Trace Quantities of Water Vapor

David Bents

This experiment is based on an early work of Langmuir (Reference 7) in which he commented that trace quantities of water vapor were effective in changing the work function of thoriated tungsten. In 1964 we repeated Langmuir's work and demonstrated that trace quantities of water vapor could be detected if oxygen was rigorously excluded from the system. No further work was done on this detector because no application was apparent at the time.

In 1969 we appreciated that a trace detector of water might be useful in a Mars lander system. The major question was whether the presence of a high pressure of  $\text{CO}_2$  (5 torr) would inhibit or mask the reaction.

To investigate this question a test system has been built with facilities for controlling  $\text{CO}_2$  partial pressure and introducing known quantities of water vapor. The system is shown in Figure 8. For operation, the system is first pumped to  $10^{-5}$  torr (via valve #1) to remove residual oxygen from the system. Dry, oxygen-free tank  $\text{CO}_2$  is expanded into the test system (via valves #5 and #2) to a pressure of 5 torr. Experiments at various relative humidities are possible by using the humidity loop shown in Figure 9. Dry  $\text{CO}_2$  is first saturated with water vapor and then the  $\text{CO}_2$  water vapor mixture is cooled to a known temperature with ice or liquid nitrogen. The  $\text{CO}_2/\text{H}_2\text{O}$  mixture reaches 100% R.H. at the ice or liquid nitrogen temperature, the excess water vapor condenses out and the remaining  $\text{CO}_2/\text{H}_2\text{O}$  gas is warmed to room temperature. The gas mixture is then expanded from one atmosphere to the 5 torr test pressure (via valves #3 and #2) to provide the proper relative humidity.

As an example we might consider how the system produces a partial pressure of  $3 \times 10^{-2}$  torr (dew point  $-50^\circ\text{C}$ ) of water vapor and a  $\text{CO}_2$  pressure of 5 torr. Returning to Figure 9, the  $\text{CO}_2$  is humidified in the water bubbler at  $20^\circ\text{C}$ , the partial pressure of water vapor is 18 torr, and the total pressure is 760 torr. The  $\text{CO}_2/\text{H}_2\text{O}$  mixture is cooled to  $0^\circ\text{C}$  and emerges at 100% R.H. with a partial water vapor pressure of 4.5 torr and a total pressure of 760 torr. The gas mixture is warmed to  $20^\circ\text{C}$  at constant pressure and the 4.5 torr of water vapor produces a



R.H. = 25%. Another way of expressing this is to give the ratio of partial pressures,

$$\frac{P(\text{H}_2\text{O})}{P(\text{total})} = \frac{4.5}{760} = 6 \times 10^{-3}.$$

If this mixture is expanded to a total pressure of 5 torr at constant temperature and both gases behave ideally, the partial pressure ratio will remain constant. The final water vapor pressure in the system will be  $3 \times 10^{-2}$  torr.

The experiments with this system have proceeded rather slowly because Mr. Bents has been spending part of his time on the Corona Discharge Humidity Detector.

Results to date indicate:

1.  $\text{CO}_2$  does not affect the work function of thoriated tungsten.
2. The work function of thoriated tungsten is greatly increased in the presence of trace quantities of water vapor.
3. Tungsten and  $\text{CO}_2$  begin to react at  $1200^\circ\text{C}$ , and the tungsten is destroyed.

To date we have not been able to operate the system as we had hoped. The problem is that we cannot heat the tungsten to  $1800^\circ\text{C}$  to desorb water vapor because of the reaction with  $\text{CO}_2$  at  $1200^\circ\text{C}$ . This is a serious problem which has not been solved to date.

#### E. Other Activities in the Laboratory

The ARPA-supported study of the relation between fatigue and postfatigue exo-electron emission is continuing. The test system for room ambient experiments is shown in Figure 9. The specimens are 1" x 7" x 0.090", 1100-0 aluminum, that have been fatigued to some fraction of their fatigue life. For a test the specimens are heated to 90°C and exposed to ultraviolet light from a quartz tube lamp. Thermally induced vacancy migration produces exo-electrons which are attracted to the positive collector.

Typical results are shown in Figure 10 where postfatigue exo-electron current is plotted as a function of the fatigue level. There seems to be a definite relation between fatigue and postfatigue exo-electron emission.

#### IV. Personnel

Students who have been supported by the grant and their present activities are listed below:

1. Donald Collins, M.S., 1963, Ph.D., California Institute of Technology, Sept. 1969. Presently Research Associate, CIT.
2. George Rozgonyi, Ph.D., 1963. Senior Staff Member, Bell Telephone Laboratories, Murray Hill, New Jersey.
3. Donald Creighton, Ph.D., 1964. Professor, University of Missouri, Rolla. (Partial NSG-458 support.)
4. Maj. C. W. Carlson, M.S., 1965. Active duty, U. S. Army.
5. Melvin Eisenstadt, Ph.D., 1965. Associate Professor, University of California, Santa Barbara.
6. John Lane, M.S., 1968. Philco Ford Company, Tucson.

7. Herman Sulsona, Ph.D., 1968. Professor and Head of the Department of Mechanical Engineering, University of Puerto Rico, Mayaguez. (Partial NSG-458 support.)
8. John Ashcraft completed an undergraduate term paper project in the laboratory. Mr. Ashcraft is now an EE graduate student.
9. W. Farwell will receive the M.S. degree in the spring of 1970. At present he is working for Hughes Aircraft in Los Angeles.

Two graduate students joined the group in June 1968. William Ott is working on the ARPA-supported exo-electron emission program. Richard Pope is working on the CO/Pd problem. Brad Frazier joined the group in June 1969; he is working on the ZnO adsorption program.

Several EE and Physics undergraduate students are working in the laboratory on a parttime basis. The draft is limiting the graduate enrollment to an increasing degree. The employment of undergraduate students helps to fill the gap and gives the students an opportunity to work in an active research laboratory.

#### V. Publications Generated to Date by Research on This Grant

S. A. Hoenig and Others

1. "Chemisorption Detector for Oxygen," *Rev. Sci. Instr.*, 35, 15 (1964), with D. Collins.
2. "Protection of Copper in High Temperature Air," *Rev. Sci. Instr.*, 35, 904 (1964).
3. "Chemisorption Detector for Hydrogen," *Rev. Sci. Instr.*, 36, No. 1, 66 (1965), with M. Eisenstadt.
4. "Change in the Thermionic Emission Current of Palladium Due to Chemisorption of Atomic and Molecular Hydrogen," *J. Chem. Phys.*, 45, No. 1, 127-132 (July 1966), with M. Eisenstadt.

5. "Beam Source for Molecular and Atomic Hydrogen," *Rev. Sci. Instr.*, 36, No. 12, 1878-1879 (1965), by M. Eisenstadt.
6. "Use of Liquid Nitrogen Cooled Shield to Protect Proton Accelerator Against Oil Vapor Contamination," *Rev. Sci. Instr.*, 37, No. 7, 977 (1966).
7. "A Low Cost, High Temperature (1300°C) Vacuum Furnace," *J. Vacuum Sci. & Technology*, 3, No. 6, 351 (1966).
8. "Detection of Hydrogen in Air by Means of Alkali Ion Current from Hot Palladium," *Rev. Sci. Instr.*, 38, No. 1, 92-94 (Jan. 1967), with C. W. Carlson and J. Abramowitz.
9. "Contamination of MOS Field Effect Transistors by Alkali Ions Emitted from Hot Tungsten or Molybdenum Filaments--Removal by Electric Fields," *Elec. Communicator*, 16-17 (Nov./Dec. 1967).
10. "Polarization Sensitivity of the RCA 6903 Photocathode Tube," *Applied Optics*, 5, No. 6, 1091-1092 (1966), with A. Cutler.
11. "Chemisorption of Oxygen on Zinc Oxide--Effect of a DC Electric Field," *Surface Sci.*, 11, 2 (1968), with J. Lane.
12. "The Electronic 'Sponge'--Selective Gas Adsorber," *Indus. Research*, (May 1968).
13. "Replication Versus Metallization for Interference Microscopy of Thin Films," *J. Vacuum Sci. & Technology*, 5, 125-126 (July/Aug. 1968), with J. Lane.
14. "Ion and Electron Currents from Hot Filaments: Effects of Alloying on Electron Emission," *Solid State Tech.*, 11, No. 12, 53 (Dec. 1968), with R. Pope.
15. "Vapor Deposition of Zinc on Glass--Effect of a Glow Discharge During Evaporation," to appear in the *J. Vacuum Sci. & Technology*.
16. "Emission of High-Energy Electrons During Alloy-Evaporation Processes on Hot Metal Filaments," to appear in *Applied Physics Letters*.

## VI. References

1. D. Smith, *Hydrogen in Metals*, Univ. of Chicago Press, 1948.
2. J. Tracy, P. Palmberg, "Structural Influences on Adsorbate Binding Energy," Carbon Monoxide on (100) Palladium," to appear in *J. Chem. Phys.*
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5. J. Connoy, P. Mark, "Electrical Conductivity Changes During Hetrogenous Catalysis," AD 678-384, (Oct. 1968).
6. I. Langmuir, *Collected Works*, 2, Pergamon Press, New York, 185 (1960).
7. J. de Boer, *The Dynamical Character of Adsorption*, Oxford Univ. Press, 224 (1968).

Figures

1. CO, H<sub>2</sub>/Pd Experimental Apparatus
2. Ion Current vs. Pressure
3. CO, H<sub>2</sub> vs. Pd Spectrum
4. Corona Discharge Humidity Detector
5. Response of Corona Discharge Humidity Detector
6. ZnO Reaction System
7. GC Flow System
8. Thoriated Tungsten Water Vapor Detector
9. Exo-Electron Apparatus
10. Exo-Electron Current vs. Time and Percent of Fatigue Life
11. Proposed Field Test System Corona Discharge Humidity Detector with Electric Wind Driver

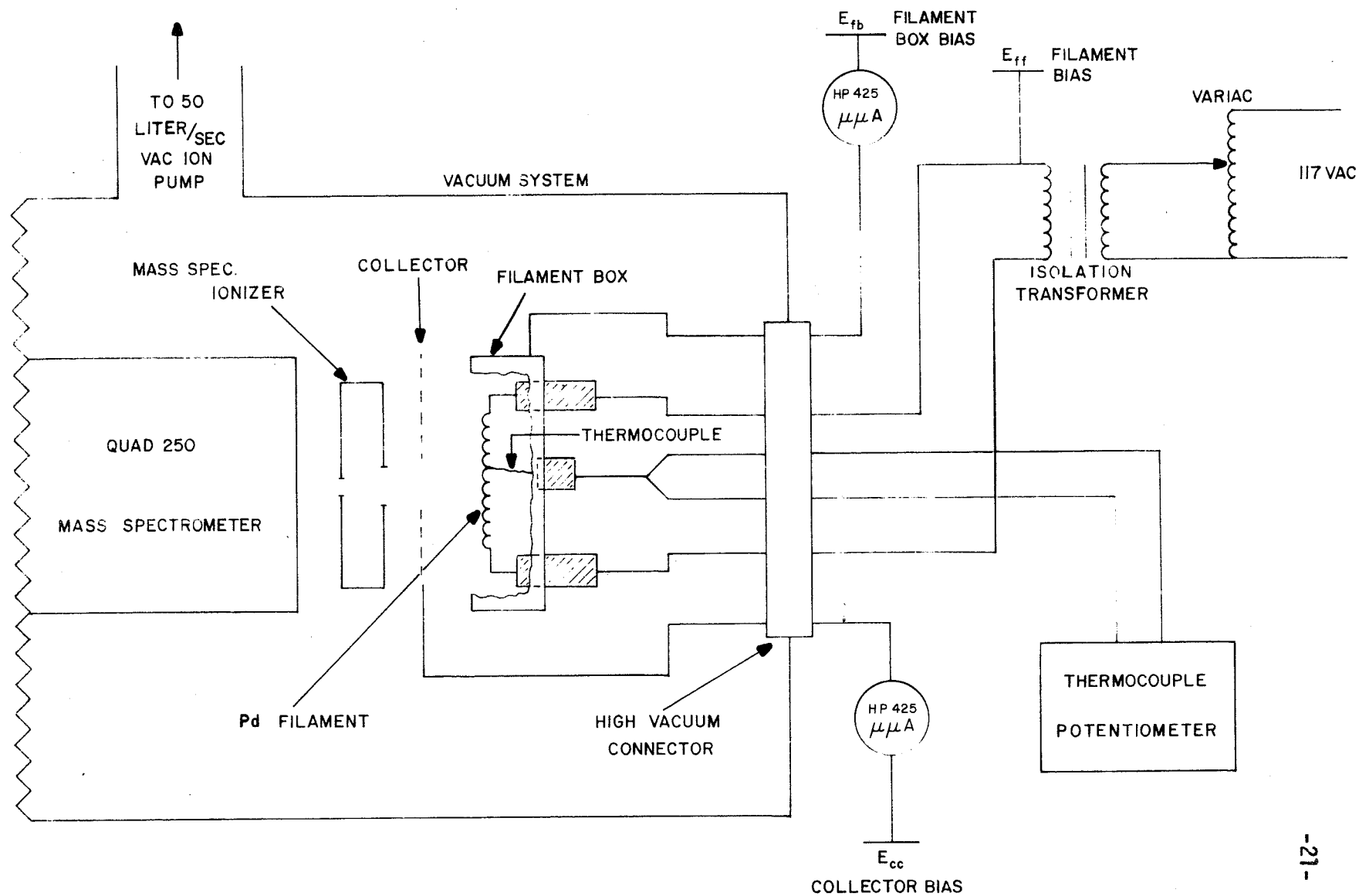


FIGURE 1  
CO, H<sub>2</sub>/Pd EXPERIMENTAL APPARATUS

CURRENT  
 $\times 10^{-12}$  AMPS

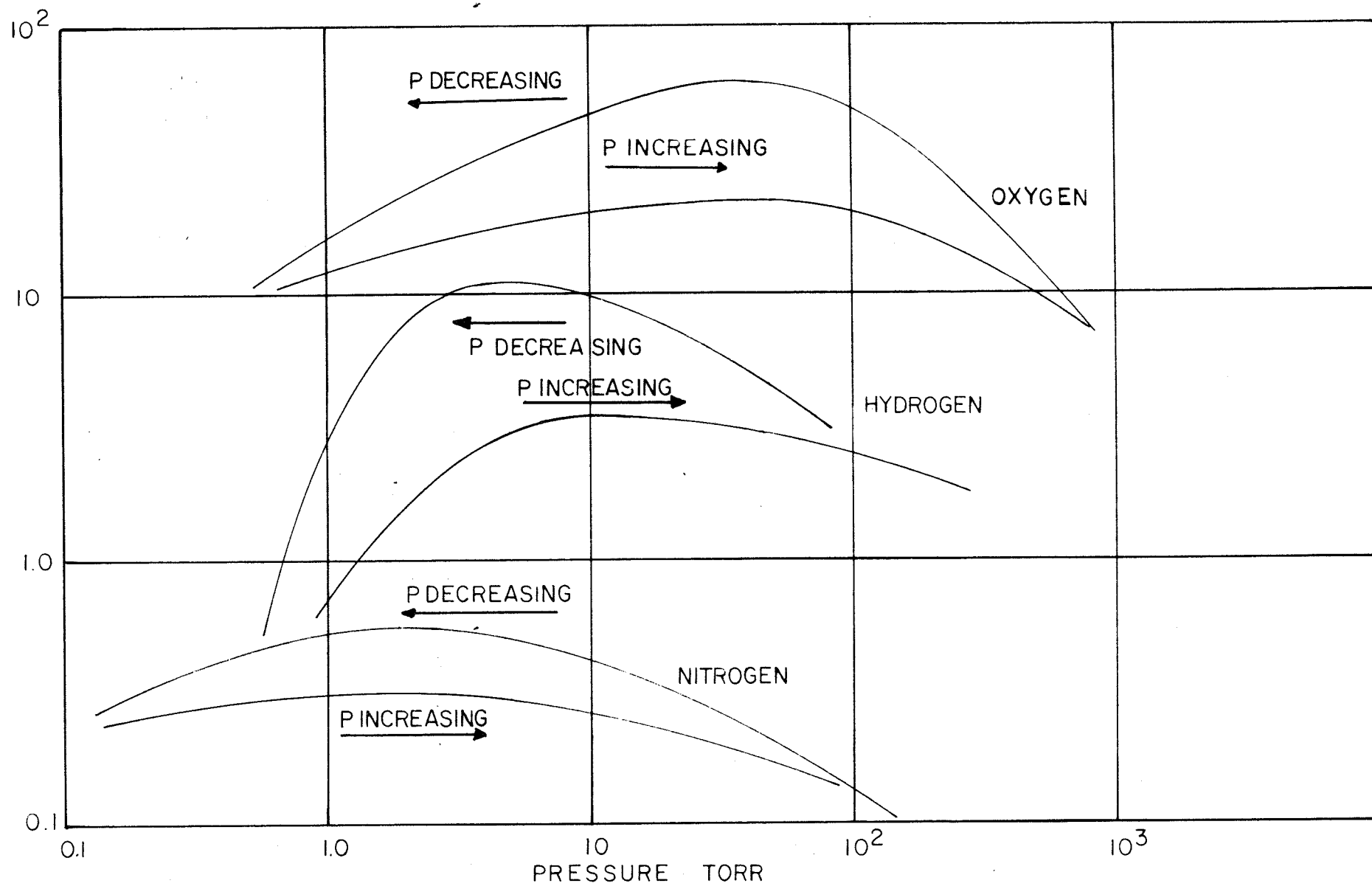


FIGURE 2  
ION CURRENT VS PRESSURE

LOGARITHMIC  
3x5 CYCLES



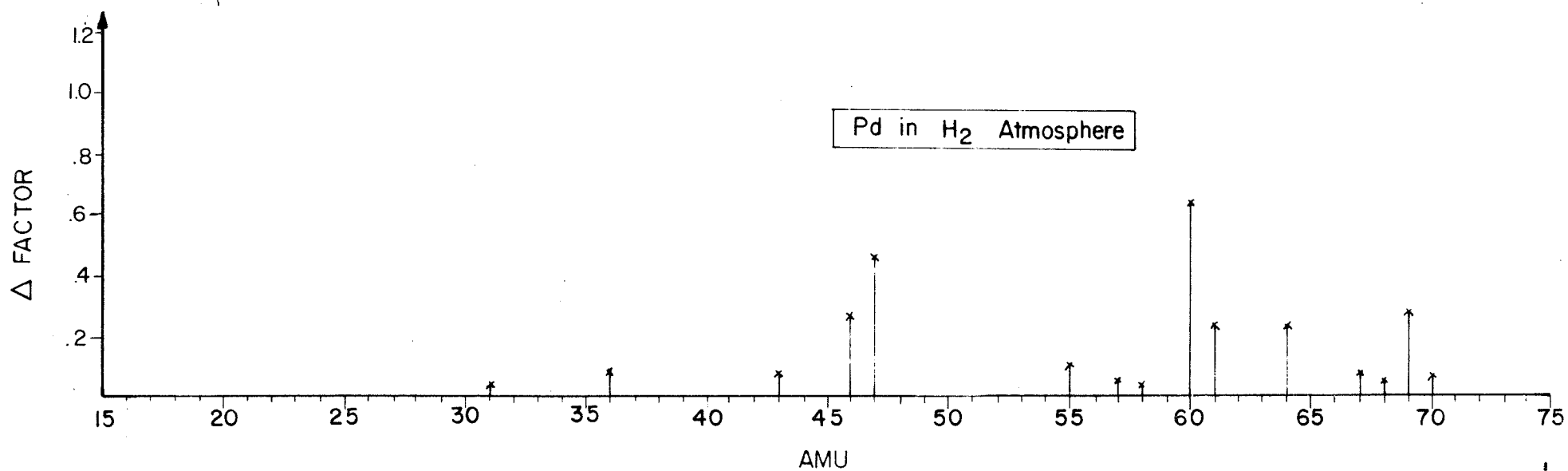
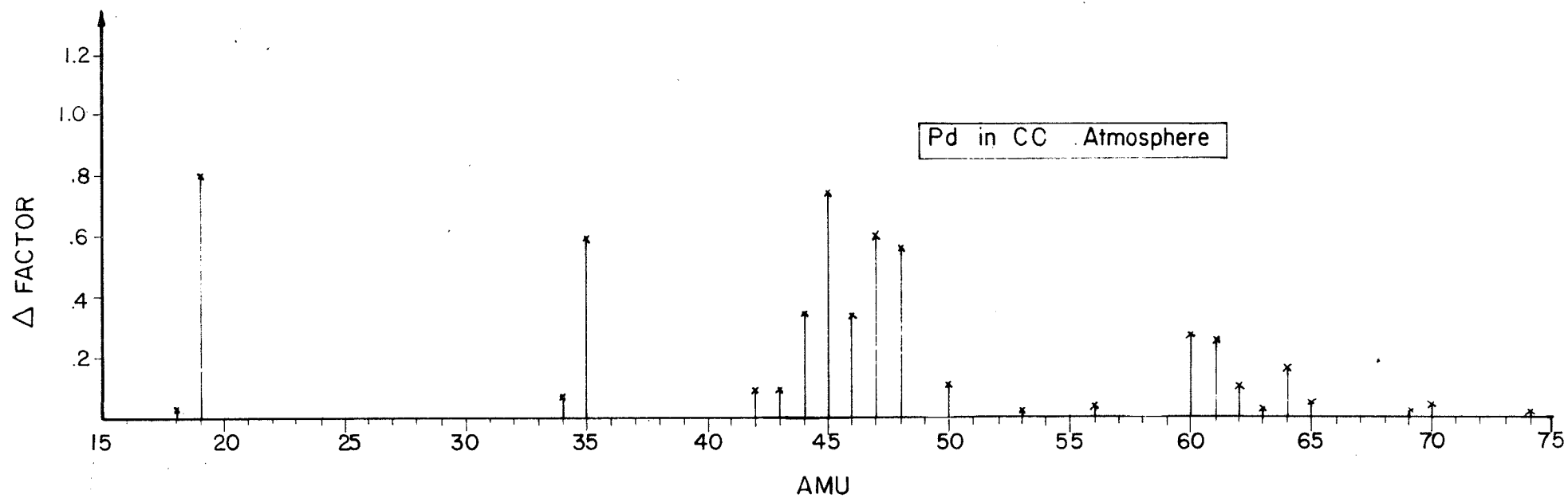


FIGURE 3. CO, H<sub>2</sub> VS Pd SPECTRUM

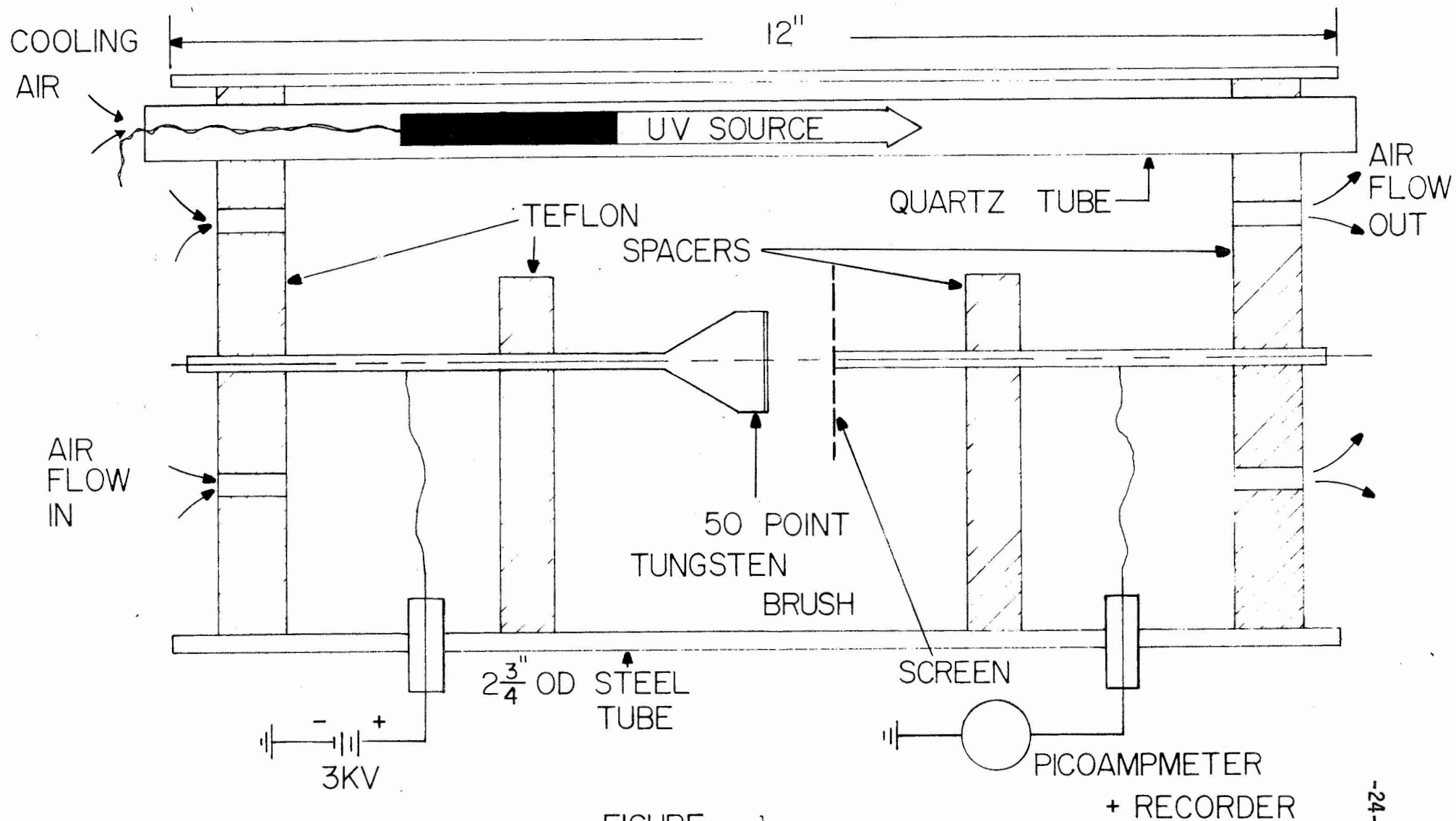
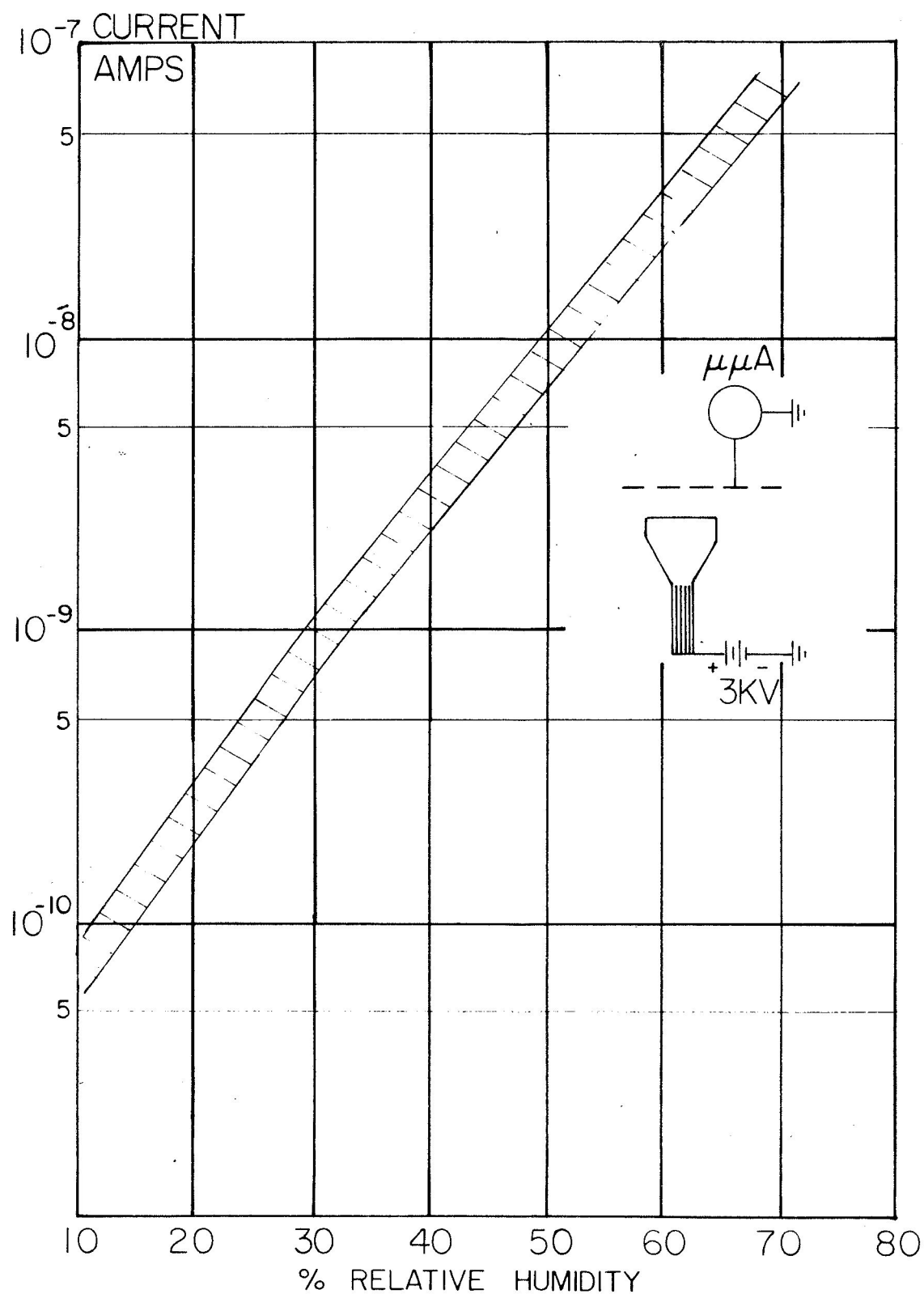


FIGURE 4  
CORONA DISCHARGE HUMIDITY DETECTOR



Semi-Logarithmic  
4 Cycles x 10 per inch

FIGURE 5. RESPONSE OF CORONA  
DISCHARGE HUMIDITY DETECTOR

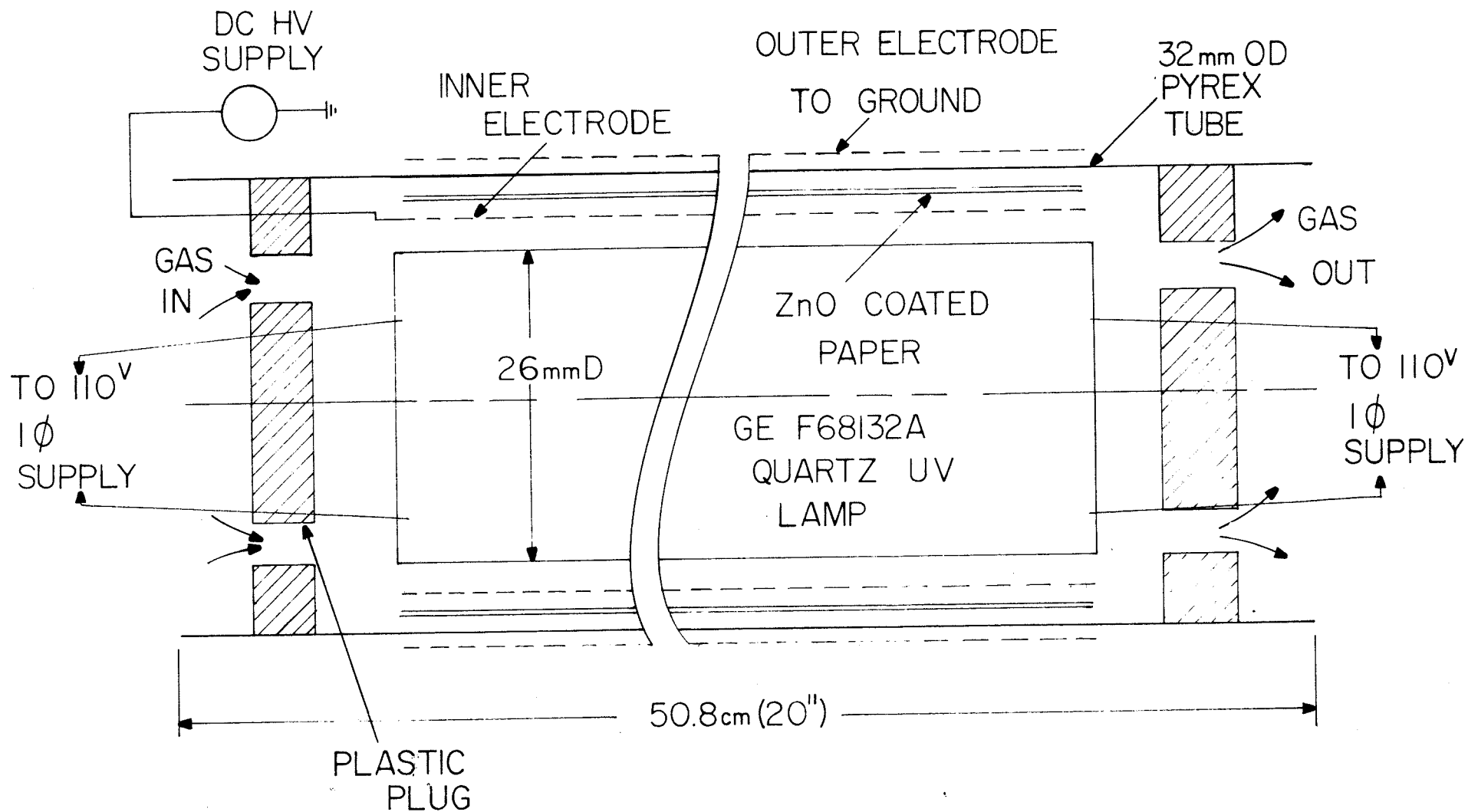


FIGURE 6  
ZnO REACTION SYSTEM

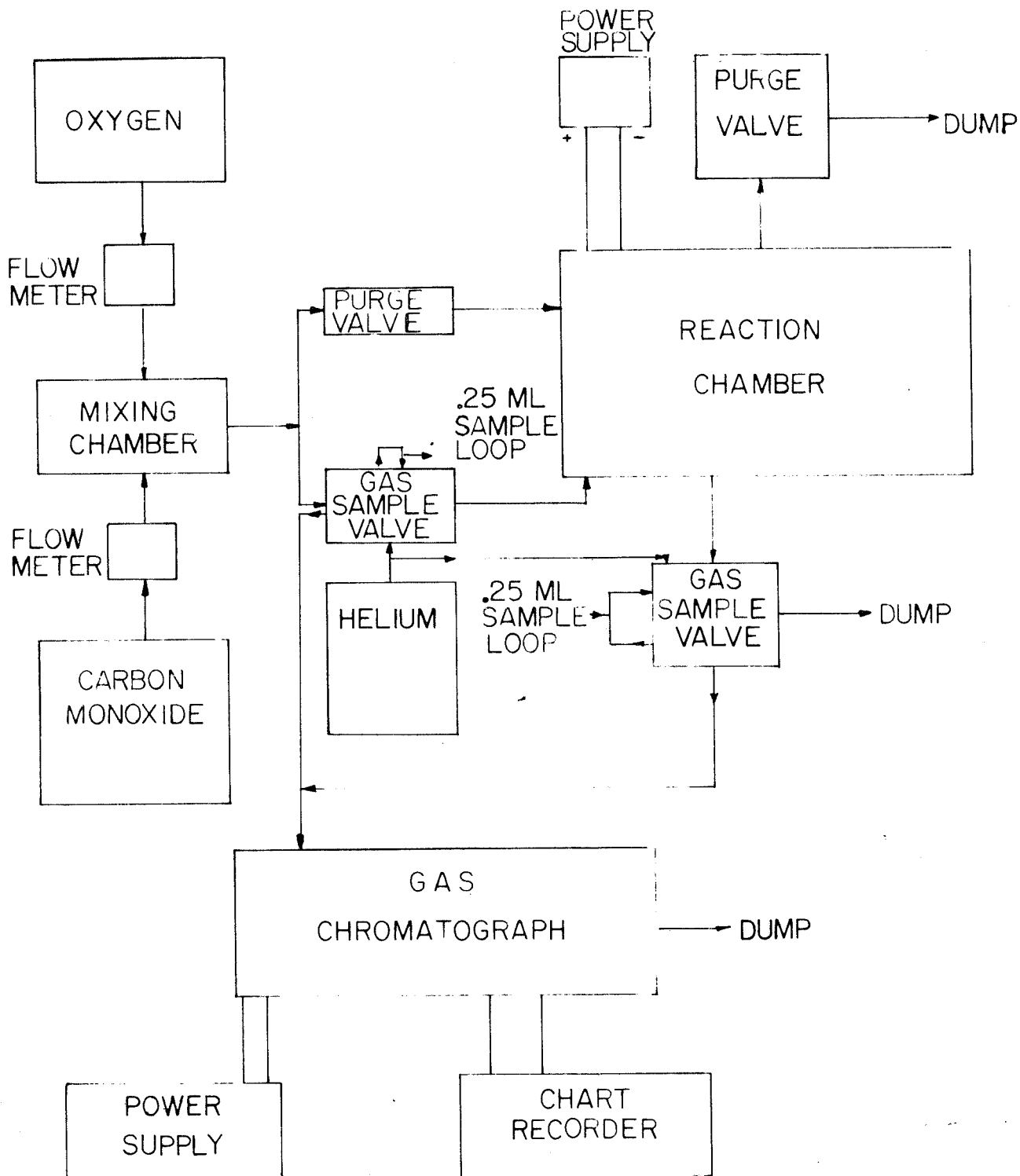


FIGURE 7  
GC FLOW SYSTEM

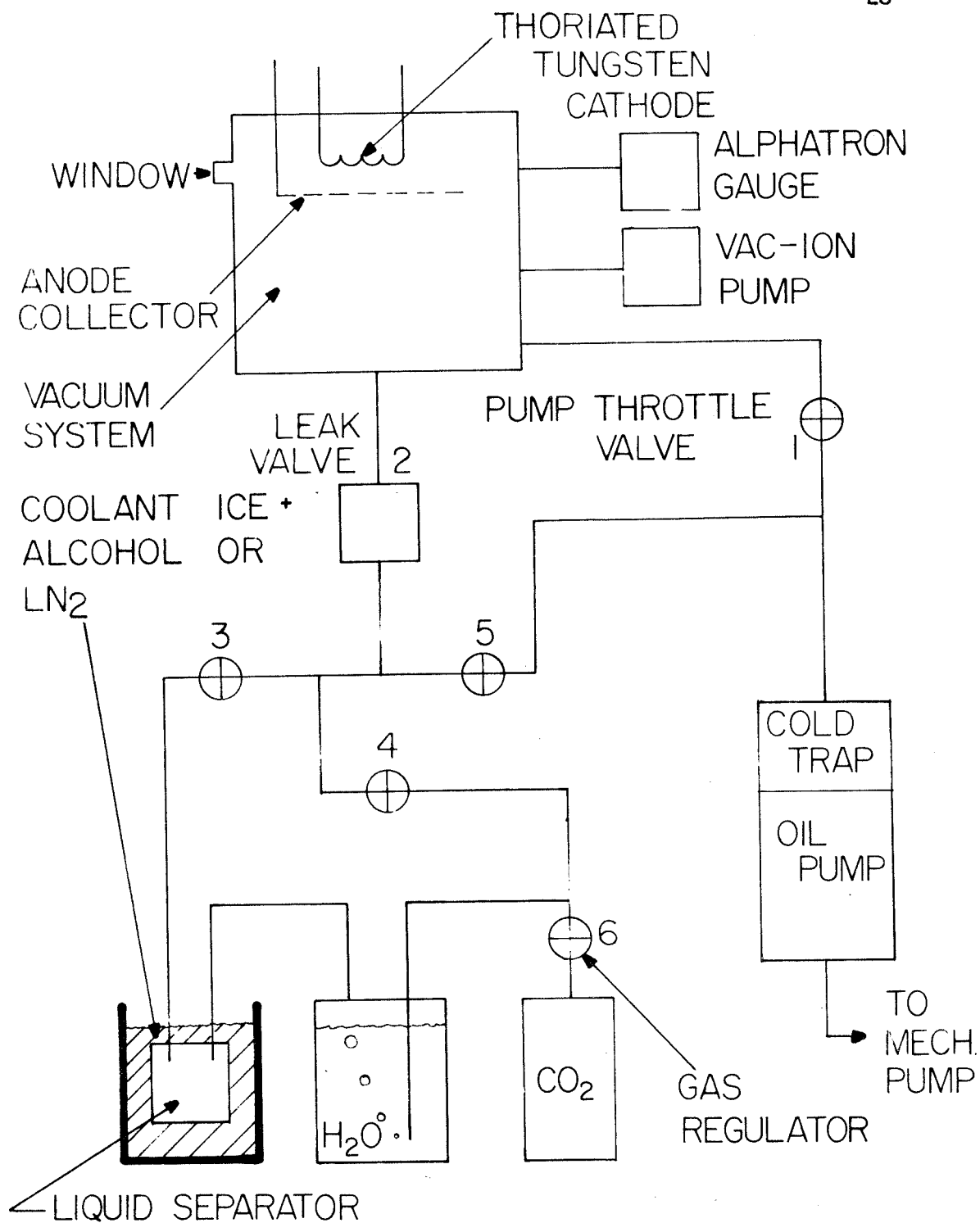


FIGURE 8  
THORIATED TUNGSTEN WATER VAPOR  
DETECTOR

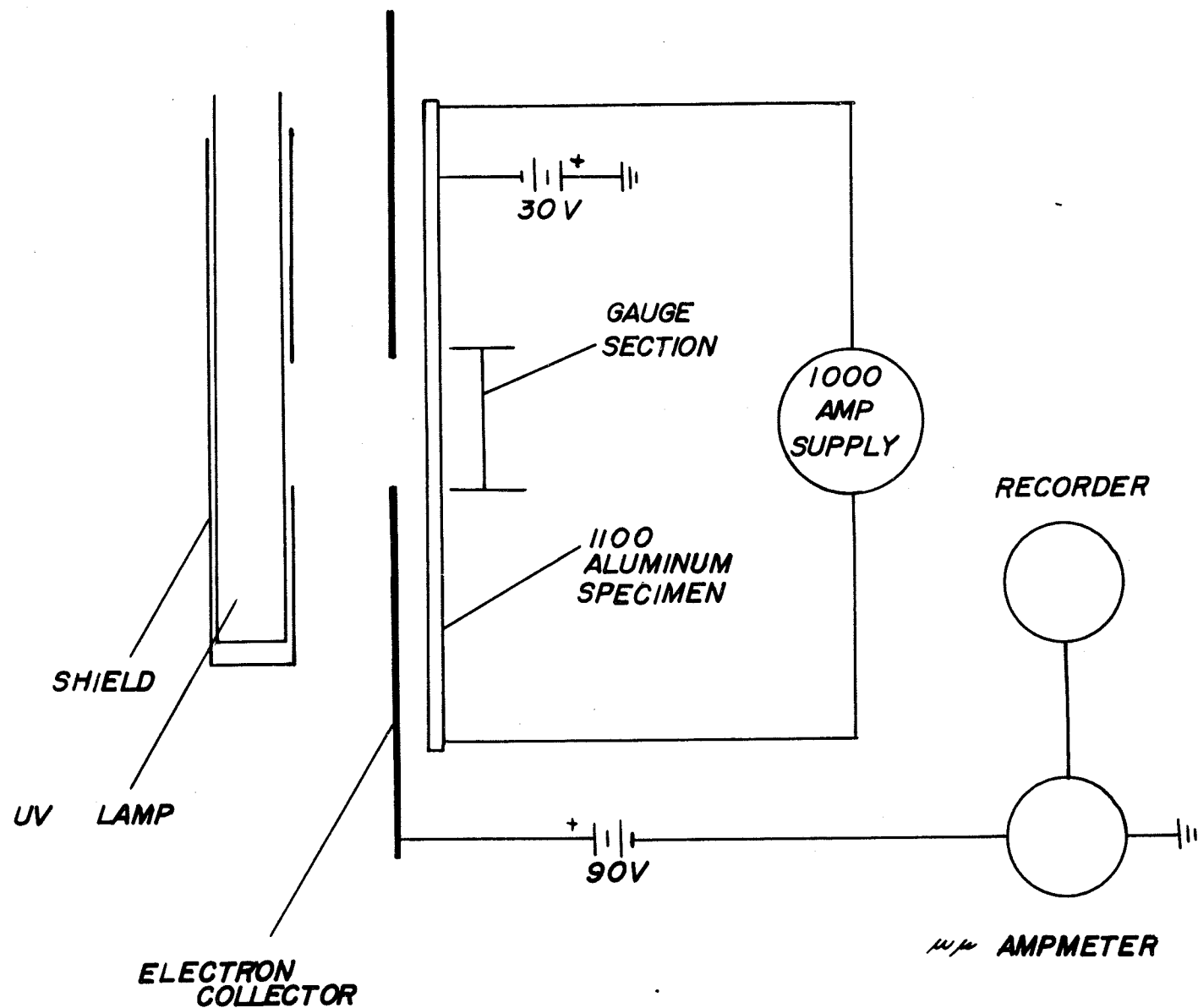
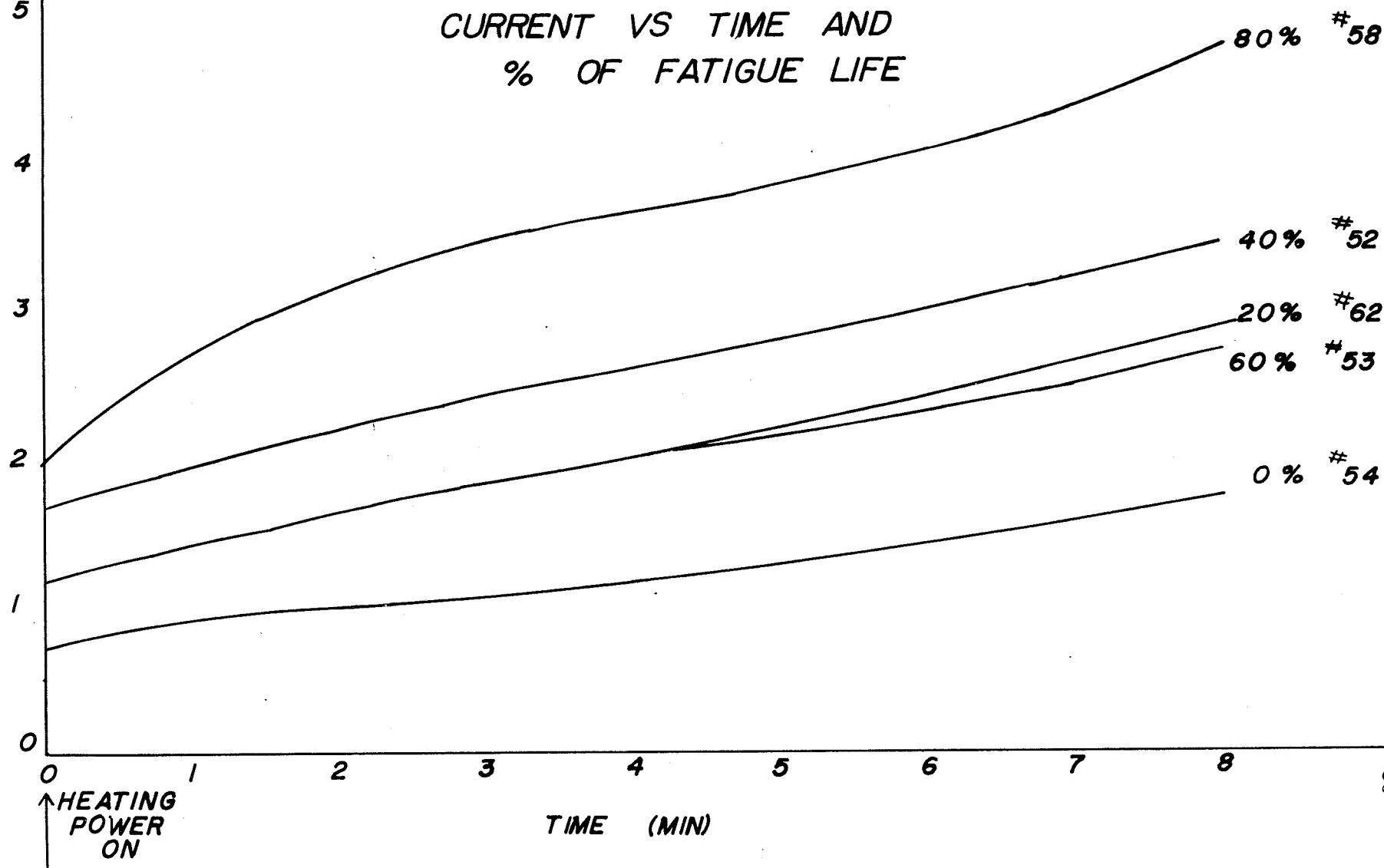


FIGURE 9 EXO-ELECTRON APPARATUS

$I \times 10^{-10}$  AMPS

FIGURE 10 EXO-ELECTRON  
CURRENT VS TIME AND  
% OF FATIGUE LIFE





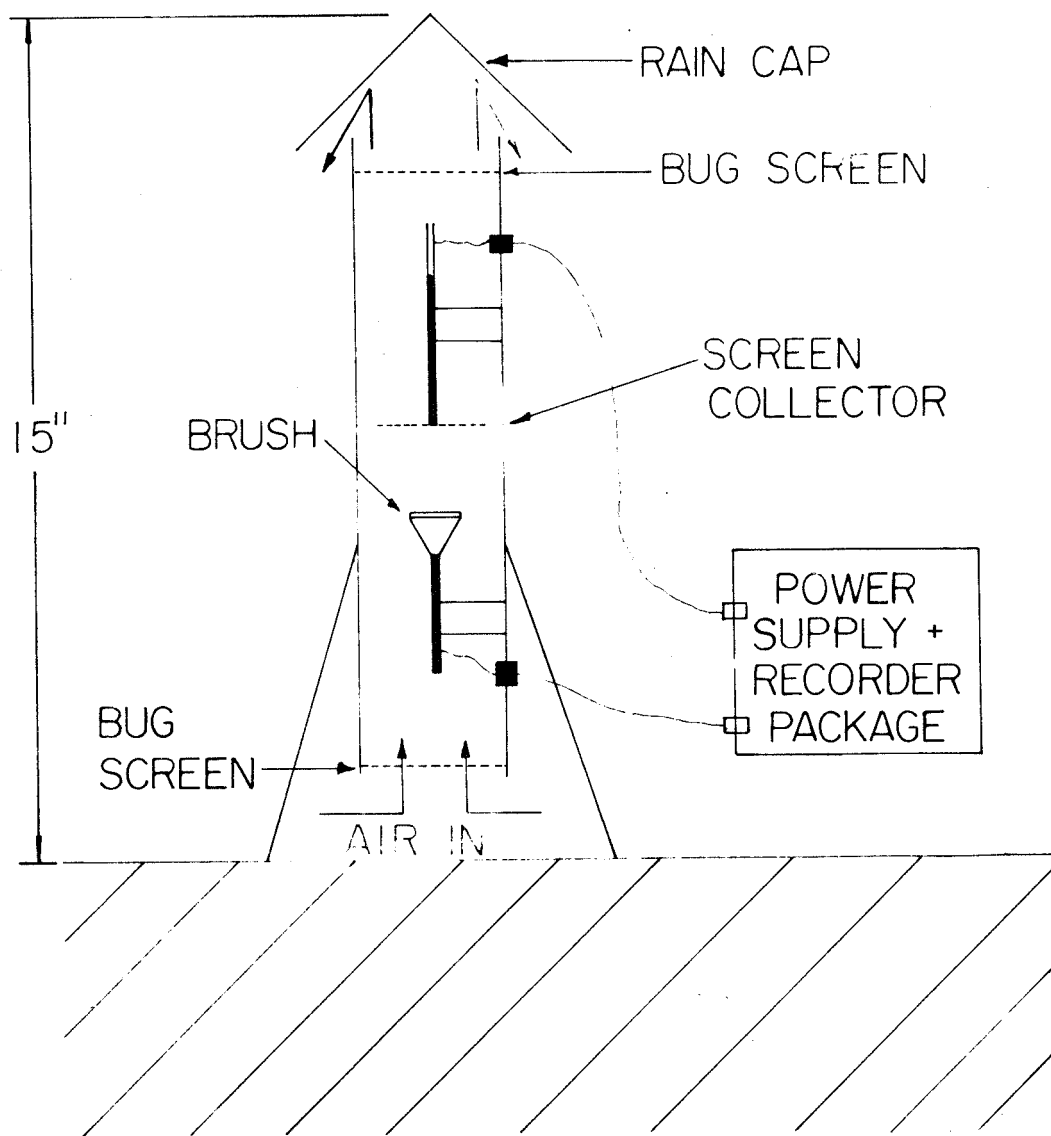


FIGURE II.

PROPOSED FIELD TEST SYSTEM  
CORONA DISCHARGE HUMIDITY  
DETECTOR WITH ELECTRIC  
WIND DRIVER